Forensic Science International 209 (2011) 133–142

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

Evaluation of selected sorbent materials for the collection of volatile organic compounds related to human scent using non-contact sampling mode

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ARTICLE INFO

Article history:
Received 3 June 2010
Received in revised form 11 January 2011
Accepted 14 January 2011
Available online 1 March 2011

Keywords:
Human scent
Odor
Scent collection
Odor delivery
Detector canine

ABSTRACT

Human scent can be collected by either contact or non-contact sampling mode. The most frequently used human scent evidence collection device known as the Scent Transfer Unit (STU-100) is a dynamic sampling device and is often used in a non-contact mode. A customized human scent collection chamber was utilized in combination with controlled odor mimic permeation systems containing five standard human scent volatiles to optimize the flow rate, collection material and geometry of the absorbent material. The scent collection method which yielded the greatest amount of volatile organic compounds (VOCs) detected included the use of a single layer of Johnson and Johnson gauze/multiple layers of Dukal gauze with the STU-100 on the lowest flow rate setting. The correlation of the resulting VOC profiles demonstrate that collection of standard VOCs in controlled conditions yielded reproducible VOC profiles on all materials studied with the exception of polyester. Finally, the method was tested using actual human subjects under optimized set of conditions.

1. Introduction

The study of human scent is of substantial interest to the forensic science community as associative evidence due to its application to scent trailing and scent identification line-ups by human scent canines. It has been known anecdotally for more than a hundred years, and much more recently, it has been shown scientifically, that every living human has a unique scent and trained canines are capable of discriminating between and locating individual people (1–5).

The ways in which the body produces this scent are not entirely understood, however it is known that the human body is surrounded by an air current filled with bacteria and dead skin cells which are constantly shed from the body. As many as 40,000 dead skin cells are shed per minute, and as they are shed the dead skin cells are caught up in such air current [1,6]. One theory suggests that as the air currents move through the environment with one's body, scent is deposited or transferred along the course [2]. Other biological materials have been used, but there is little scientific evidence to support or refute these theories. For the purpose of this study, only primary human scent odor is of interest, as primary odor is characterized as the volatile organic compounds originating from the body, which are constant over time and environmental conditions, and are not affected by outside influences such as diet, illness, or application of topical products [3].

Types of VOCs present above human skin include aliphatic hydrocarbons, aldehydes, ketones, alcohols, fatty acids, and esters [2,3,7–13]. A study performed by Curran et al. sampled the hand odor of 60 individuals. The most commonly occurring compounds (occurring in more than 30% of individuals) included furfural, 2-furanmethanol, propanedioic acid–dimethyl ester, phenol, 6-methyl-5-hepten-2-one, nonanal, octaonic acid–methyl ester, dodecane, decanal, nonanoic acid–methyl ester, hexanedioic acid–dimethyl ester, undecanal, tetradecane and geranyl acetone [3]. In order to deliver such compounds in a realistic and reproducible manner during non-contact sampling, controlled odor mimic permeation systems (COMPS) were created (discussed below).

Human scent may be collected and presented to a canine in several manners. The canine may be presented with the actual scent article, such as a personal article left by the perpetrator at a crime scene. This approach is less commonly used, as it may destroy or contaminate other evidence. Alternatively, scent may be collected by swiping a sterile piece of gauze across the surface of the scent article or by having the gauze held in the palms of the suspect. Again, this may bring about contamination or removal of other evidence. The method of interest to this study does not necessitate direct contact with the scent article, but instead it employs a non-contact sampling procedure. By using non-contact sampling procedure, the investigators do not risk contamination or removal of trace evidence.

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doi:10.1016/j.forsciint.2011.01.010

In this research a "scent vacuum", referred to as the Scent Transfer Unit (STU-100) was utilized. The STU-100 is a field portable, dynamic airflow, sampling device for contact or non-contact sampling of human scent. It consists of a fan that draws air through a patented pad holder, creating a vacuum. This is attached to a Teflon-coated hood which has been designed to hold a piece of collection material. As the STU-100 is swept over the subject or object of interest, air is drawn toward the device, collecting any VOCs present to the gauze pad. The pad may then be presented to the canine in order to initiate a search or returned to a laboratory for analysis and/or storage. The STU-100 has the benefit of being non-intrusive, and thus does not disturb or destroy evidence [4,14]. This device is currently being used by hundreds of police departments in the United States.

In one study, it was shown that the STU-100 could even be used to collect human scent evidence from post-blast debris. The residual human scent was collected from the debris onto an absorbent pad using the STU-100. This pad was presented to trained human scent canines, which were then able to trail correctly to the target 82.2% of the time [15].

Volatile organic compounds, such as those in human scent, tend to be preserved well in textiles because of their porous nature, but the extent of the ability to trap or release VOCs depends on the type and nature of the material used [16]. In the United States, the FBI uses Johnson and Johnson gauze pads, a blend of cotton with rayon and polyester. Other scent-collection protocols use alternative collection materials to collect and store human scent. The Dutch National Police use King's Cotton, a pure cotton gauze, while other research studies with human scent and human scent canines have used Dukal cotton gauze [2,4,15,17].

Prada et al. compared the non-contact sampling of human subjects using the STU-100 to contact sampling with different materials. It was observed that collection with the STU-100 lacked quantity and variety of organic compounds compared to direct contact sampling. It was also shown that the type of compounds detected was highly dependent on the type of material used for collection. The investigation by Prada et al. was limited to living human subjects and did not include experiments conducted using standard compounds [18], however due to the inherent variability of human scent, sorbent materials are best evaluated using standard compounds.

Eckenrode et al. conducted a preliminary evaluation of the ability of the STU-100 to trap and release standard compounds. The group verified that the device was capable of trapping and releasing compounds from cotton material at ambient temperatures, however the efficiency was rather poor. The evaluation was conducted using volatile organic compounds not necessarily associated with the composition of human scent [14], thus further research is needed to validate this device as a forensic tool. Further evaluation and optimization of the STU-100 as a non-contact scent collection tool is required using standard compounds representative of human scent volatiles conducted in order to improve the efficiency of the device.

Also, in the study performed by Eckenrode et al., the standard compounds were either injected onto the sorbent materials directly or were introduced by a stream of gas containing the VOCs. It is imperative to develop a delivery system for these compounds in a manner that realistically mimics the emission or scent from the human body.

Scent and scent canines were first addressed by the court system as early as 1893 in *Hodge v. State*, in which a trained canine followed the scent of a suspect from the crime scene to the home of the subject [19]. This evidence was deemed admissible; however since this first case this concept has come before the courts many times. In order for scientific evidence to be admitted in court, the scientific technique must pass either a *Kelly-Frye* hearing or a *Daubert* hearing depending on the state in which the case is being tried [20,21]. In a recent 2005 case, the state of California conducted a *Kelly-Frye* hearing regarding scent evidence collected with the Scent Transfer Unit. It was questioned whether the STU-100 met the standard of reliability required for *Kelly-Frye*. The evidence was ultimately found admissible [22]. In 2009, scent evidence collected with the STU-100 underwent a *Daubert* hearing in *US v. Wade*. The court determined that the scent evidence was admissible as it exceeded the threshold of reliability under Evidence Rule 702 and *Daubert* [23]. In order to validate the assertion of reliability of the STU-100 in scent evidence collection, further studies and optimization should be carried out.

2. Materials and methods

2.1. Materials

The scent collection materials tested included Dukal brand, sterile, 2″ × 2″, 8 ply gauze pads (DUKAL Corporation, Syossett, NY); bleached, desized, mercerized cotton print cloth; spun polyester type 54; viscose rayon challis (Test Fabrics Inc., West Pittston, PA); and Johnson and Johnson brand, sterile 2″ × 2″ gauze pads (Johnson and Johnson, Skillman, NJ). The permeable polymer bags used included high density, polypropylene bags, 3″ × 4″ × 2 MIL and low density, polyethylene bags, 3″ × 3″ × 1.5 MIL (Veripak, Atlanta, GA). Five standard compounds found as common components of human scent [3,18] were used, including 2-furanmethanol, 99%, furfural, 99% (Sigma–Aldrich, Inc., St. Louis, MO); 6-methyl-5-hepten-2-one, 99%, hexanedioic acid, dimethyl ester, 99+% (Acros Organics, NJ); and Tetradecane, 99+% (Aldrich Chemical Company, Inc., Milwaukee, WI). HPLC grade methanol (Fisher Scientific, Fair Lawn, NJ) was used to clean materials and vials. Human subjects were to wash the hands and forearms with Natural, Clear Olive Oil Soap (Life of the Party, North Brunswick, NJ, USA).

Samples were collected with a dynamic headspace sampling device, the Scent Transfer Unit (STU-100) (Big T LLC, Haw River, NC) using non-contact sampling mode. The air flow rate passing through the STU-100 was calculated using the Testo 405-V1 Thermo-Anemometer (Testo Inc, Sparta, NJ). The absorbent materials were removed from the STU-100 and placed into 10 mL clear, screw top glass vials with PRFE/Silicone septa (SUPELCO, Bellefonte, PA). Samples were extracted using solid phase microextraction with Divinylbenzne/Carboxen/PDMS fibers (SUPELCO, Bellefonte, PA).

2.2. Sampling chamber

A human scent collection chamber was designed to reduce background contamination during human scent sampling. An enclosure large enough to accommodate a single human subject was constructed (Fig. 1). A metal cover was attached and sealed securely to the top of the chamber, while the other walls of the chamber allowed small amounts of air to pass. A section of the metal cover was removed and replaced with a grating. A filter was placed over the grating, and the forced induction device over that. The chamber was designed in such a manner to utilize positive air flow, that is, as clean air entered the chamber through the top, contaminated air is forced out through the small openings. Several filters were compared to optimize background VOC removal from the chamber. These included the Filtrete Air cleaning Filter, Ultra Allergen, 20″ × 20″ × 1″ (3 M Construction and Home, St. Paul, MN), WINIX Replacement Carbon Pre-Filters, and WINIX Replacement HEPA Filter (WINIX Inc., Hoffman Estates, IL).

2.3. Sampling utilizing the Scent Transfer Unit (STU-100)

The controlled odor mimic permeation (COMP) devices were sampled with a non-contact, dynamic sampling device, the Scent Transfer Unit (STU-100) (Fig. 2). The hood was fitted with a stainless plate with opening for the gauze 2″ in diameter, as was designed by Prada et al. [18]. The vacuum of the STU pulls air through the gauze pad, which acts as a trap for the odorants onto the collection material.

2.4. Methods

2.4.1. Optimization of the sampling chamber

The effectiveness of the filters used in the sampling chamber to reduce VOCs present in the background was evaluated using standard compounds commonly found in human scent. Twenty-five microliters of the liquid compounds were spiked onto Dukal cotton gauze, which was then sealed into permeable bags. The bags were then positioned under the forced induction device and above the filters. Due to the air flowing from the forced induction device, the scent compounds were forced through the filters and into the chamber. The relative amounts of compound entering the chamber were determined by exposing the SPME fiber inside of the chamber, then desorbing the collected compounds into the GC/MS.

For validation, a series of blank samples were taken from inside and outside of the chamber using the STU-100. The STU-100 was run for 1 min on the medium

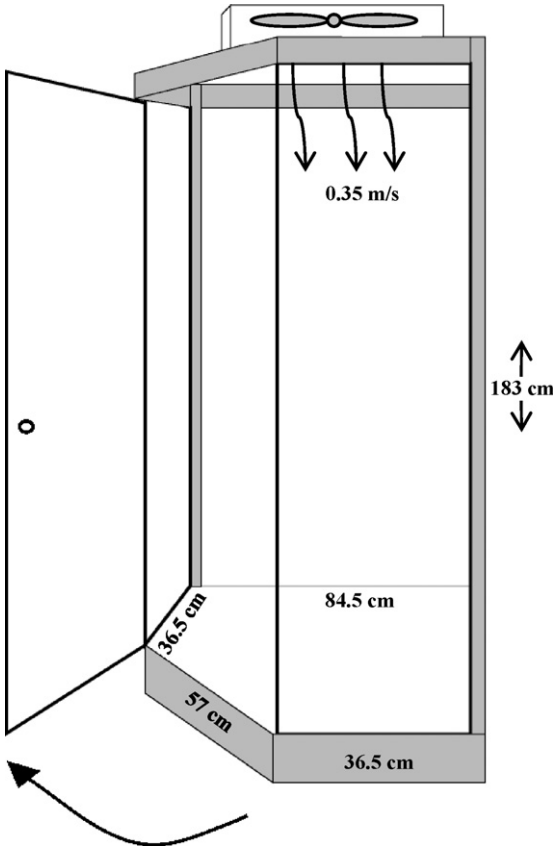

Fig. 1. Schematic of human scent collection chamber.

airflow setting while collecting the odorants onto Dukal brand sterile gauze. The fan on the chamber was run for 6 h prior to collection to remove contaminants from the air contained inside of the chamber. The odor content was analyzed using SPME-GC/MS (as described later in the text), and the type and amount of human scent compounds collected were compared.

2.4.2. Creation of controlled odor mimic permeation system (COMPS)

Controlled odor mimic permeation system (COMPS) were created to deliver standard compounds to the STU-100 at controlled rates in a reliable and reproducible manner and in a manner that mimics the slow and constant emission of scent from the human body. Harper developed canine training aids prepared in a similar manner for explosive and drug detection canines. Target drugs or explosive odorants were spiked onto sterile gauze and placed into a permeable, polymer bag

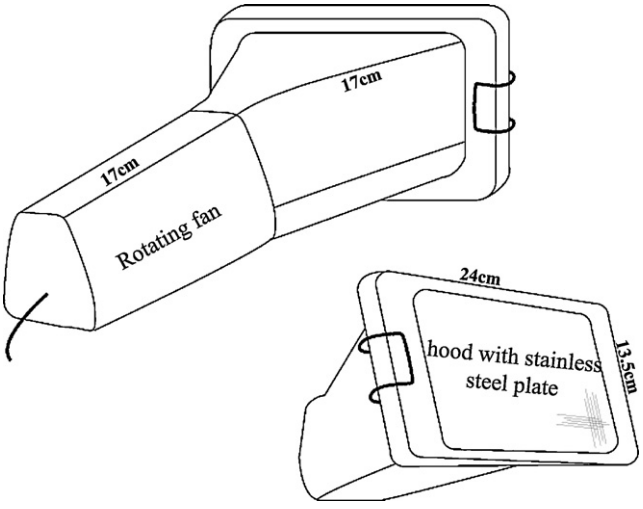

Fig. 2. Diagram of the Scent Transfer Unit.

Table 1
Standard compounds chosen for study.

Compound	Functional group	Molecular weight	Literature cited
6-Methyl-5-hepten-2-one	Ketone	126.2	[3–6,11,16]
Furfural	Aldehyde	96.08	[4,16]
Tetradecane	Aliphatic	198.39	[4,6,11,16]
2-Furanmethanol	Alcohol	98.1	[4,16]
Hexanedioic acid, dimethyl ester	Fatty acid, methyl ester	174.19	[4,6,16]

and heat sealed. The target odorants diffused through the plastic membrane at known and reproducible rates to be used as training aids for canines [24]. In the current study, the COMPS were spiked with compounds previously reported in literature to be VOCs emanating from the human body, and are used as a means of introducing a flow of compounds to the STU-100 at controlled rates.

The COMPS were prepared using Dukal brand, sterile gauze pads which were sealed into either high density, polypropylene bags or low density, polyethylene bags. Five standard compounds found as common components of human scent [3,18] were used, including 2-furanmethanol, furfural, 6-methyl-5-hepten-2-one, hexanedioic acid, dimethyl ester, and Tetradecane (Table 1). All five compounds chosen for the study have good chromatographic resolution and sensitivity on the GC/MS (Fig. 3).

The COMPS were prepared by spiking standard compounds separately onto gauze pads. The dissipation of each compound from the material and through the polymer bag was determined by gravimetric analysis. The amount of each compound remaining versus time was plotted and the rate of dissipation was determined by the slope of the line.

2.4.3. Pre-treatment of collection material

The collection and release of compounds onto five types of collection materials were compared: Dukal brand gauze pads, cotton material, polyester material, rayon material and Johnson and Johnson brand gauze pads. Prior to sampling, these materials were cleaned for analytical purposes because, though the materials may be sterile when they are removed from the package, they still contain human scent VOCs [3]. To remove such compounds, the material was placed in clean glass vials, spiked with 1 mL of methanol, and baked in an oven for 45 min at 105 °C. These materials were then placed inside a 10-mL glass vial and analyzed using the SPME-GC/MS method described later in the text, materials that were proven to be free of human scent compounds were used for further experimentation.

2.4.4. Collection of standard compounds with the STU-100

For sampling of the standard compounds, a cleaned piece of the material to be evaluated was placed on the face of the STU-100, held in place by a stainless steel plate, as described previously. The compounds were sampled in triplicate with the STU-100, holding it one inch above the controlled odor delivery devices and sampling for 60 s. All sampling with the STU-100 took place in the human scent

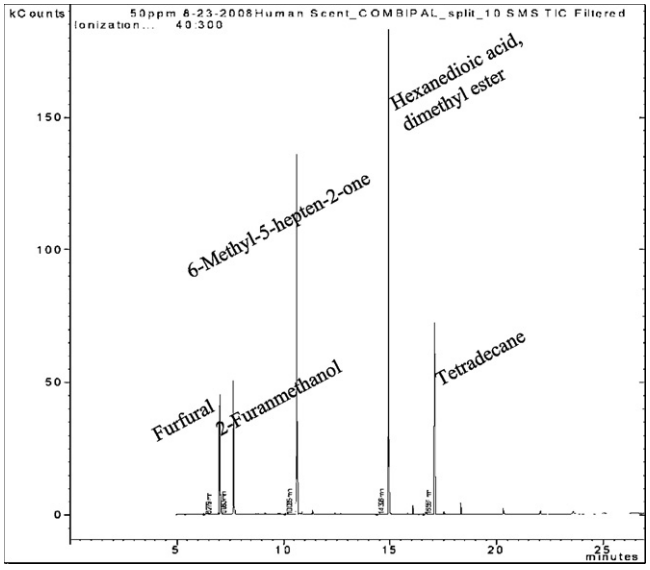

Fig. 3. Chromatogram of 50 ppm solution of standard compounds.

collection chamber. An environmental blank was collected from inside the chamber before sampling. Between sampling, the STU-100 was cleaned by wiping all surfaces with alcohol pads. Each of the following four air flow speeds was used for each fabric: high (9), medium (5), low (0) or no air flow. After 60 s of sampling, the material was immediately removed and placed back into the same vial from which it came. The rate of air flow through the vacuum for each combination of material and flow rate was measured using an anemometer. The number and quantity of VOCs detected from each material/flow rate combination was compared.

To determine whether a greater number of material layers would enhance or impede scent collection, multiple layers of material of the same material were assessed. Layers of the collection material were placed on top of one another and onto the STU-100. Following sampling, the layers of materials were removed from the STU-100 and placed into separate vials for extraction. For sampling, the lowest flow rate setting was used, as this was previously determined during the prior experiment to be the optimum collection flow rate. The flow rates through the layered material were monitored using an anemometer.

2.4.5. Sampling of human subjects with the STU-100

Scent from four human subjects, 2 male and 2 female, was collected in triplicate with the optimum collection parameters determined previously (low flow rate, Johnson and Johnson gauze, two layers). The scent samples were taken from the palm of one hand of each subject. An environmental blank was collected from inside the chamber before the human subject was sampled. Prior to sampling, the subject was asked to wash his/her hands with a fragrance-free soap and allow them to air dry. The subject sampled him/herself inside of the human scent collection chamber for 1 min. The subject was instructed to pick up the STU-100 with one hand and sample the palm of the other. The subject was asked to remove the piece of gauze from the STU-100 using cleaned tweezers after sampling and place it into the vial. The same hand was sampled for each replicate sample, and the subject was instructed to not touch anything between replicate samples. The STU-100 was cleaned with sterile alcohol pads between samplings.

2.4.6. Extraction and analysis of samples

The same extraction procedure was followed as has been optimized in previous studies for the extraction of collected hand odor profiles [3]. Following sample collection, the materials were placed into 10 mL screw top vials and allowed to equilibrate for 24hrs. The headspace was sampled for 21 h using DVB/Carboxen/PDMS SPME fibers. The compounds were thermally desorbed from the SPME fibers and analyzed on the GC/MS with a HP-5MS column. The injector temperature was held at 250 °C and the column oven was held at 40 °C for 5 min, and then increased to 250 °C over 23 min. The quantities of compounds detected by the GC/MS were determined using five point calibration curves (5, 10, 20, 50 and 100 ppm) for each compound of interest.

2.4.7. Methods for statistical evaluation

The source of variation between samples was evaluated using one-way ANOVA analysis. One-way ANOVA is used to determine whether variation between samples is due to random error in measurement or to a single controlled factor, thus ANOVA can test whether altering the controlled factor, such as flow rate or material, produces a significant difference in the amount of compound collected compared to differences found in replicate samples [25].

Cluster analysis is used to group sets of objects based on similarity and was used to determine the relatedness of the replicate samples taken inside and outside of the human scent collection chamber. A cluster tree or dendrogram was created using Minitab 15 Statistical Software (Minitab Inc., State College, PA). The *y*-axis measures the similarity of the observations on the *x*-axis, with 100 being exactly the same and 0 being completely dissimilar. The observations on the *x*-axis were the replicate samples taken in each location. The more similar the replicate samples are to one another for each location, the more reproducible [25].

Spearman rank correlation was conducted to determine the similarity of pairs of samples based on the type and ratio of human scent compounds in the sample. For this type of analysis, the amount of compound collected is converted into ranks based on the quantity and type of compound present, and the differences, d_i, between the ranks are calculated. The correlation coefficient, r_s, is determined by Eq. (1).

$$r_s = 1 - \frac{6\sum_i d_i^2}{n(n^2-1)} \quad (1)$$

The correlation coefficient can range from −1 to 1, with 0 being no correlation and 1 being exactly positively correlated and −1 being exactly negatively correlated (meaning the compounds are the same, but the ranking is opposite). When the absolute value of the correlation coefficient is above the critical value, the null hypothesis is rejected and it can be said that there is a correlation [25]. In the case of the comparison of the correlation between two human scent odor profiles, a score of 1 indicates the profiles are the similar and a score of −1 indicates profile compounds are the same but the ratios of such compounds may be different.

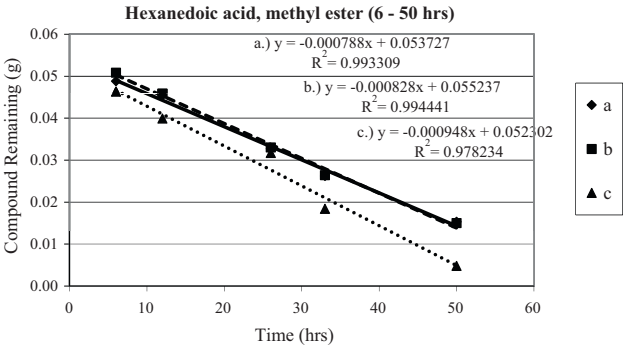

Fig. 4. Plot of the dissipation of hexanedioic acid, dimethyl ester from gauze material through polymer bag over time in triplicate.

3. Results and discussion

3.1. Creation of controlled odor mimic permeation (COMP) devices for human scent compounds

The rate of dissipation of VOCs through the 1.5 MIL low density, polyethylene bags was measured for each compound on Dukal gauze, cotton material and polyester material using gravimetric analysis. For the gravimetric analysis, the scent collection material to be tested was spiked with one of the volatile compounds, sealed into a polyethylene bag, and weighed. The mass was recorded over time and plotted as amount of compound remaining versus time. The slope of the linear portion of this line was considered to be the dissipation rate, expressed in mg/s. This experiment was done in triplicate and the dissipation rates from each trial were averaged. An example is given in Fig. 4 for the dissipation rate determination of hexanedioic acid, dimethyl ester. Note that only the linear portion of the graph (6–50 h) is used to determine the dissipation rate.

To assess variation, ANOVA analysis was conducted on the dissipation rates for each material type and compound. The *F*-value for the variation between compounds was 33.5 with a *F*-critical value of 2.35, while the *F*-value for the variation between materials was 5.99 with a *F*-critical value of 3.49. This shows that there was significant variation between dissipation rates from each of the three materials, but there was a much greater variation between the dissipation rates of each compound. As can be seen in Fig. 5, the dissipation of the compounds from Dukal gauze was slightly faster than that from the other materials. In order to maintain consistency in study, further experimentation was conducted using only Dukal gauze.

For the purposes of future experimentation, it is advantageous to minimize the range of dissipation rates, making the rates of dissipation of all compounds as similar as possible. Therefore, it was considered necessary to use permeable bags of different thicknesses and makeups to minimize the distribution of dissipation rates, thus 2 MIL, high density, polypropylene and 1.5 MIL, low density, polyethylene bags were also tested. The rates of dissipation through each of these bags were compared. Based

Table 2
Optimum permeable bag. Low density, 1.5 MIL (LD); high density, 2 MIL (HD).

Compound	Rate (mg/min)	LD or HD
6-Methyl-5-hepten-2-one	0.361 ± 0.003	HD
Furfural	0.394 ± 0.028	HD
Tetradecane	0.422 ± 0.073	HD
2-Furanmethanol	0.616 ± 0.083	LD
Hexanedioic acid, dimethyl ester	0.855 ± 0.090	LD

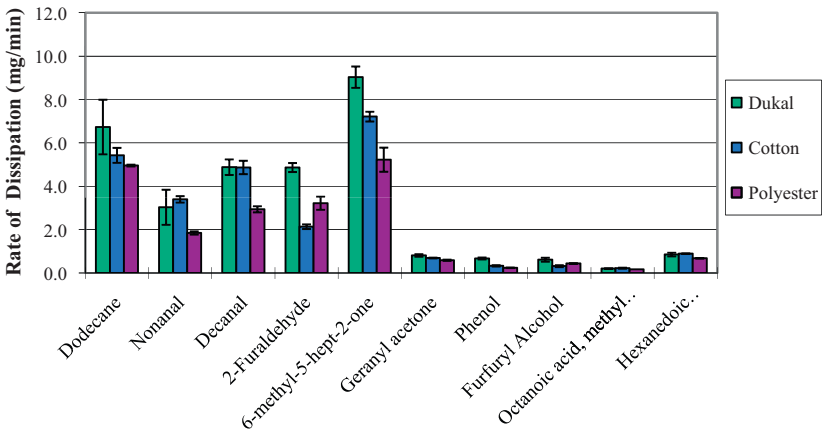

Fig. 5. Dissipation rates of standard compounds through seal polyethylene bags, 1.5 MIL from three materials.

on the results, the "optimum" permeable bag was selected for each compound individually. The selection of the optimum permeable bag was based on reducing the range of dissipation rates, i.e. compounds that dissipated quickly from the low density bags were placed in high density bags to slow down the dissipation rate. The resulting dissipation rates for each compound are listed in Table 2.

3.2. Improvement of reproducibility for the collection of human scent

The best possible filter for the human scent chamber system was chosen based on the results shown in Fig. 6. The air filter alone reduced a significant amount of the compounds compared to no filter (Single Factor ANOVA: $F_{calc} = 26.8$, $F_{crit} = 5.99$). The difference between all treatments also differed significantly (Two Factor ANOVA: $F_{calc} = 5.42$, $F_{crit} = 5.14$). The addition of the carbon filter reduced a large portion of the furaldehyde, hexanedioic acid, dimethyl ester and tetradecane, and reduced a small portion of the furfuryl alcohol. However, the addition of the HEPA filter actually increased the amount of compounds present in the chamber for all four compounds. Based on these results, the air and carbon filter combination was selected to be utilized for the remainder of the experiments presented in this study.

The STU-100 was used to collect scent samples of the background compounds found inside and immediately outside the human scent collection chamber. Both sets of samples were taken indoors, in a laboratory setting, under the same environmental conditions. The samples taken immediately outside of the chamber contained 10 known human scent compounds, as listed in Fig. 7, while samples taken inside the chamber in the same fashion contained only 6 human scent compounds. The six compounds detected inside the chamber were reported by Curran et al. as high frequency human scent compounds [3]. There was also a significant reduction (approximately 66%) in the total amount of human scent compounds inside the chamber compared to air from outside the chamber (Fig. 7). The human scent collection chamber successfully removed a significant quantity of human scent-related volatiles found in the air, and thus enhanced the quality of non-contact dynamic airflow sampling by decreasing background contamination.

A cluster analysis was performed in order to compare the similarity of the volatile background profiles of the same four replicate samples collected both inside and outside the chamber. Fig. 8 is a dendrogram representing such analysis. The more similar the profiles of two samples, the lower they are connected in the dendrogram. The most similar samples are Ch1, Ch2, and Ch3; three samples taken from inside the chamber. While it did not group with the other three, the forth sample from inside the chamber (Ch4) was far more similar to Ch1, Ch 2, and Ch3 than it was to samples Out1 and Out4 from outside the chamber. Samples Out1 and Out4 were the least similar to the entire group and to each other. The dendrogram indicates that the samples taken inside the chamber were more similar to one another, and thus more reproducible, than the replicates taken outside of the chamber. This confirms the importance of the use of the human

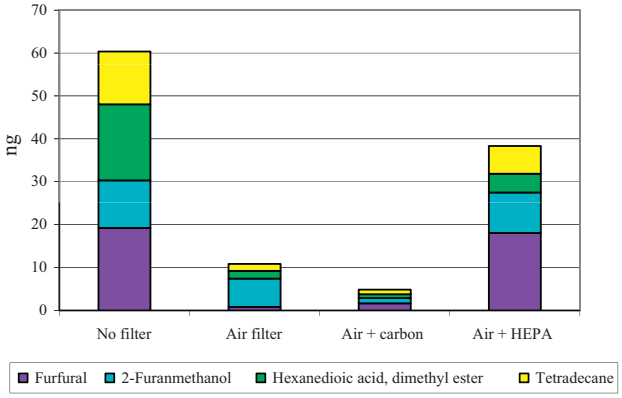

Fig. 6. Quantity of standard compounds collected using SPME-GC/MS from inside of the chamber after passing the compounds through filters outside the chamber.

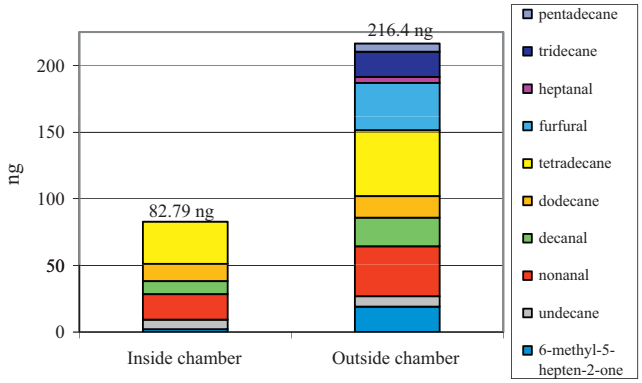

Fig. 7. Human scent compounds found in blank air samples taken inside and outside the chamber.

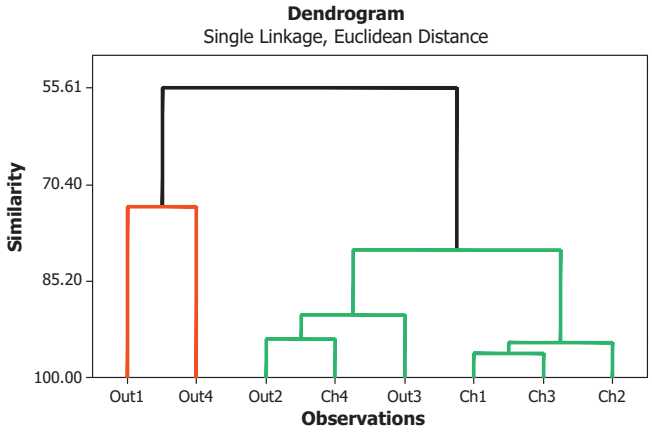

Fig. 8. The cluster tree depicts the similarity between replicate samples taken in inside the human scent collection chamber (Ch) and outside the chamber (Out).

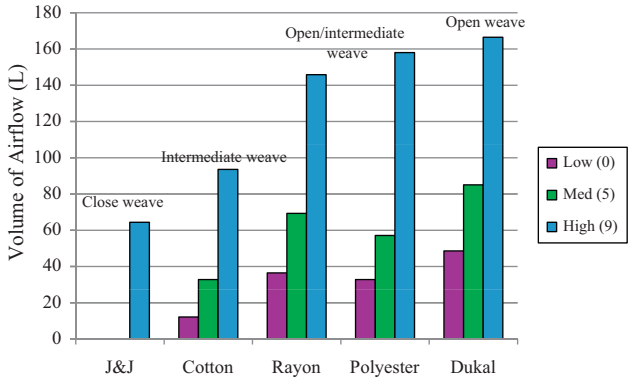

Fig. 10. Quantity of air pulled into device after 60 s of sampling for different setting and material combinations. Flow rate settings on the STU-100 included 0, 5 and 9 for low, medium and high flows. Flow rate for the low and medium flow rates were less than 0.1 m/s and could not be determined accurately.

scent collection chamber during experimentation, as a more reproducible background environment is obtained using the chamber than simply sampling a subject indoors.

3.3. Scent collection material and flow rate comparison

The flow rate of the air drawn past the material and into the STU-100 was measured for each setting/material combination, i.e. flow rates 0, 5, 9 and off with materials polyester, rayon, cotton, Johnson and Johnson gauze, and Dukal gauze. Macroscopically, Dukal gauze has the most open weave, followed by the polyester and rayon materials which have relatively open weaves, then by the cotton material which has an intermediate weave, and then Johnson and Johnson which has the tightest weave (Fig. 9). In Fig. 10, a pattern can be observed relating the weave of the material to the obstruction of airflow into the STU-100. The Johnson and Johnson gauze impeded the airflow into the device more than the other materials of interest while Dukal gauze allowed for the greatest airflow.

The total amounts of the standard compounds collected from the headspace of each material after sampling with the STU-100 at different airflow settings are shown in Fig. 11. In general, the STU-100 used with no vacuum yielded the least amount of compounds collected from the headspace of all materials, and the low (0) and medium (5) flow rate settings performed marginally better than the highest setting (9), but this was not a statistically significant difference (determined by ANOVA). The breakthrough of compounds through the collection material during sampling most

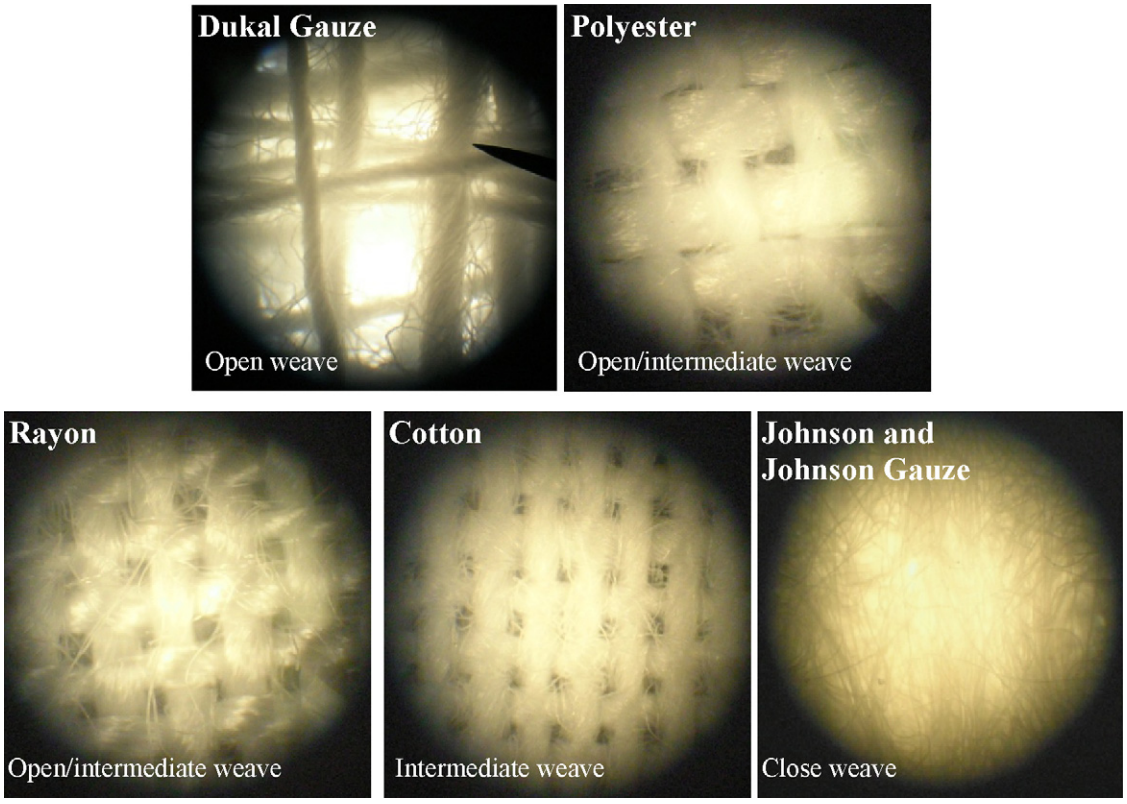

Fig. 9. Microscopic images comparing the weaves of the collection materials at 4×.

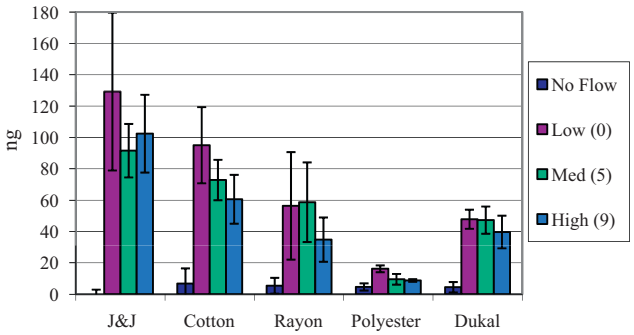

Fig. 11. Total amount of standard compounds trapped and released from various materials at low (0), medium (5), high (9) and no flow rates in triplicate.

likely played a role in the lesser amount of compound collected at the higher flow rate, meaning at the higher flow rate, the compounds were drawn quickly past the collection material without being deposited onto the material.

Table 3 lists the amount of each standard compound recovered at each material/flow rate combination. When comparing collection material performance, overall, the polyester material trapped and/or released the least amount compounds compared to the other four materials tested. Across the four tested airflows, no material studied here collected the complete suite of VOCs. 2-Furanmethanol and 6-methyl-5-hepten-2-one were not seen at any flow rate using the polyester material. This difference may be attributed to the molecular structure of polyester, as it differs from the molecular structure of the other materials as it contains a long chain synthetic polymer with backbone held together by ester bonds with no free –OH groups. Cotton has a cellulosic backbone containing many free hydroxyl groups; rayon is a synthetic cellulose-based material, structurally similar to cotton. The Dukal brand gauze is made wholly of cotton, while the Johnson and Johnson brand is blend of cotton, rayon and polyester. The data suggests that the trapping or the release of the standard human scent compounds may be related to the molecular structure of the collection material; however collection is also likely affected by additional factors. When Figs. 10 and 11 are directly compared, it could be suggested that the amount of compound trapped and/or released is also closely related the measureable flow rate of air into the STU-100. For example, the Johnson and Johnson gauze impedes airflow the most and also traps/releases the greatest overall amounts of compounds among the five materials tested. From this data, it can be concluded that the molecular structure as well as the weave of the material have major effect on the ability to trap and release volatile compounds using the STU-100.

The similarity of replicate samples of each collection material tested was evaluated using Spearman Rank Correlation. This statistical analysis was done in order to determine the level of correlation (reproducibility) between samples taken with the STU-100 of the standard compounds discussed above for each collection material. Spearman Rank Correlation has previously been used to compare the similarity between human scent samples [9,20,23]. For $n = 5$, the match/no match threshold is ± 0.900 at the significance level of $P = 0.05$. All pairs with scores higher than ± 0.900 can be said to be matches, and are found in bold in Table 4. All pairs with scores lower than ± 0.900 are non-matches, and are listed in italics in Table 4. The scores for pairs of replicate samples from the same material are found in the highlighted boxes. Dukal gauze was the only material studied to achieve a perfect correlation among the replicate samples. The scores between all replicates from the same material are 0.981 or higher for the remaining materials with the exception of polyester. These results demonstrate that collection of VOCs from the COMPS in controlled environmental conditions yield reproducible profiles on all materials studied with the exception of polyester. The scores for polyester show quite poor correlation between the triplicates, meaning the profiles are not as reproducible. Of all of the total possible pairs (104 pairs in total), 44 pairs or 42%

Table 3
Quantity (ng) of standard compound collected at each material/flow rate combination.

	No flow	Speed 0	Speed 5	Speed 9
J&J				
Furfural	0.00	0.19 ± 3.69	1.39 ± 1.34	0.56 ± 1.26
2-Furanmethanol	0.00	2.60 ± 3.19	2.15 ± 0.75	1.01 ± 1.45
6-Methyl-5-hepten-2-one	1.58 ± 0.27	2.95 ± 1.26	3.87 ± 2.29	1.52 ± 0.70
Hexanedioic acid, dimethyl ester	2.94 ± 1.46	90.05 ± 46.2	61.10 ± 16.3	68.75 ± 24.7
Tetradecane	0.59 ± 1.81	33.52 ± 19.4	23.09 ± 4.34	30.60 ± 0.71
Cotton				
Fufural	0.61 ± 0.83	2.16 ± 0.97	1.12 ± 0.11	0.33 ± 0.35
2-Furanmethanol	1.83 ± 3.17	11.24 ± 1.24	9.00 ± 0.98	6.60 ± 0.51
6-Methyl-5-hepten-2-one	0.65 ± 1.13	6.33 ± 1.44	6.14 ± 0.31	3.28 ± 2.99
Hexanedioic acid, dimethyl ester	1.37 ± 1.58	75.35 ± 34.2	55.86 ± 25.2	50.38 ± 13.7
Tetradecane	2.32 ± 3.29	0.00	0.74 ± 3.43	0.00
Rayon				
Furfural	0.00	0.00	1.38 ± 2.39	2.92 ± 2.54
2-Furanmethanol	0.00	0.97 ± 1.69	0.95 ± 1.65	0.00
6-Methyl-5-hepten-2-one	0.61 ± 1.05	0.00	0.00	0.00
Hexanedioic acid, dimethyl ester	0.00	39.78 ± 23.1	26.47 ± 5.90	19.88 ± 15.28
Tetradecane	4.81 ± 0.93	15.63 ± 7.23	29.91 ± 11.1	12.04 ± 1.66
Polyester				
Furfural	4.66 ± 0.61	4.55 ± 0.32	4.53 ± 0.30	0.43 ± 0.44
2-Furanmethanol	0.00	0.00	0.00	0.00
6-Methyl-5-hepten-2-one	0.00	0.00	0.00	0.00
Hexanedioic acid, dimethyl ester	0.00	5.39 ± 0.42	0.82 ± 0.48	5.17 ± 0.50
Tetradecane	0.00	6.30 ± 2.10	4.19 ± 3.37	3.17 ± 0.53
Dukal				
Furfural	0.15 ± 0.52	0.85 ± 0.30	0.54 ± 0.52	0.18 ± 0.26
2-Furanmethanol	0.00	5.17 ± 0.50	5.28 ± 0.10	4.45 ± 0.06
6-Methyl-5-hepten-2-one	1.71 ± 0.37	2.06 ± 0.86	4.76 ± 1.08	0.90 ± 0.33
Hexanedioic acid, dimethyl ester	2.62 ± 2.65	39.77 ± 5.76	34.62 ± 6.41	28.86 ± 9.39
Tetradecane	0.00	0.00	2.07 ± 5.74	5.30 ± 4.44

Table 4
Spearman Rank Correlation scores for all combinations of materials with replicate samples.

	JJ1	JJ2	JJ3	Cot1	Cot2	Cot3	Ray1	Ray2	Ray3	Poly1	Poly2	Poly3	Duk1	Duk2	Duk3
JJ1	1.000	**0.981**	**0.984**	**0.956**	**0.930**	*0.894*	**0.995**	**0.992**	**0.968**	*0.750*	*0.612*	*0.409*	**0.943**	**0.941**	**0.948**
JJ2		1.000	**0.999**	*0.886*	*0.850*	*0.803*	**0.993**	**0.999**	**0.994**	*0.728*	*0.637*	*0.391*	*0.867*	*0.863*	*0.874*
JJ3			1.000	*0.891*	*0.855*	*0.808*	**0.996**	**0.999**	**0.996**	*0.771*	*0.701*	*0.514*	*0.872*	*0.868*	*0.879*
Cot1				1.000	**0.996**	**0.984**	**0.923**	**0.913**	*0.853*	*0.614*	*0.384*	*0.159*	**0.999**	**0.999**	**1.000**
Cot2					1.000	**0.994**	*0.891*	*0.879*	*0.811*	*0.554*	*0.307*	*0.078*	**1.000**	**0.999**	**0.999**
Cot3						1.000	*0.849*	*0.834*	*0.759*	*0.468*	*0.211*	*-0.021*	**0.990**	**0.990**	**0.987**
Ray1							1.000	**0.999**	**0.981**	*0.723*	*0.593*	*0.337*	**0.907**	**0.904**	**0.913**
Ray2								1.000	**1.000**	**0.931**	*0.534*	*-0.150*	*0.895*	*0.892*	*0.902*
Ray3									1.000	*0.866*	*0.655*	*0.000*	*0.831*	*0.827*	*0.839*
Poly1										1.000	*0.189*	*-0.500*	*0.582*	*0.581*	*0.601*
Poly2											1.000	*0.756*	*0.343*	*0.340*	*0.364*
Poly3												1.000	*0.117*	*0.114*	*0.139*
Duk1													1.000	**1.000**	**1.000**
Duk2														1.000	**1.000**
Duk3															1.000

were above the ±0.900 threshold and considered matches. The rayon material and the Johnson and Johnson gauze yielded very similar scent profiles to one another, as did the Dukal gauze and the cotton material likely due to the similarity of their molecular structure. None of the pairs with polyester, which does not have a similar structure to any of the materials, were above the 0.9 threshold. This again, indicates that the molecular structure of the collection material plays a role in which compounds are trapped and released during collection.

In summary, Dukal gauze was the only material studied to achieve a perfect correlation among the replicate samples and polyester material was determined to contain the least reproducible collected VOC profile. Also, the Johnson and Johnson gauze trapped and/or released the most total of the five standard compounds; however, no one material collected the total suite of VOCs at every flow rate measured and a greater amount of the furfural and 2-furanmethanol was collected by the cotton material and the Dukal gauze. This could be related to the hydrogen bonding between the aldehyde and the alcohol and the free hydroxyl groups on the cellulosic backbone of the cotton materials. The Johnson and Johnson gauze performed marginally better than the cotton material, this could be because the Johnson and Johnson gauze is a blended material with multiple fiber chemistries and thus provides more options for molecular interactions.

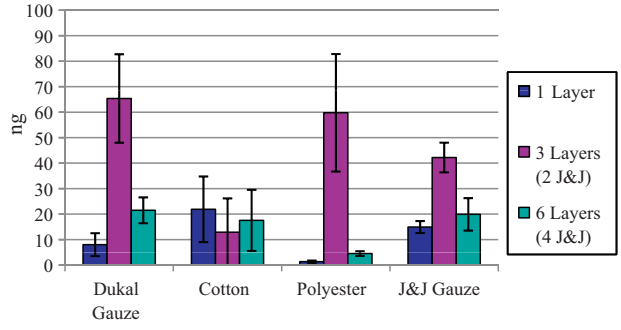

Fig. 12. Total compound trapped and released from layered materials.

3.4. Multiple material layers

It was seen in the previous section that the material with the tightest weave, and thus the greatest propensity to impede airflow into the STU-100, yielded the greatest total amount of standard human scent compounds in the headspace. For this reason, multiple layers of each of the different collection materials were tested to determine if additional material and additional reduction of the airflow would improve scent collection further. Single, three and six layers of a single material, polyester, cotton or Dukal, were tested, as well as, single, two and four material layers of the Johnson and Johnson gauze were tested. Due to the thickness of the Johnson and Johnson gauze, it was not possible to use more than four layers at a time. The samples were collected in triplicate at the low flow rate (0), as this was previously determined to be the optimum flow rate.

The greatest amount of compound was collected from the headspace of samples collected onto intermediate number of gauze layers (Fig. 12). Using ANOVA, the amount of compound collected at the intermediate number of layers was significantly different than the amount collected at the other layers for all materials except cotton (Table 5). A single layer of material is more

Table 5
F values for two factor ANOVA without replication ($F_{crit} = 6.944$).

	F_{calc}	Significant difference?
Dukal	10.312	Yes
Cotton	0.837	No
Polyester	11.965	Yes
J&J	84.615	Yes

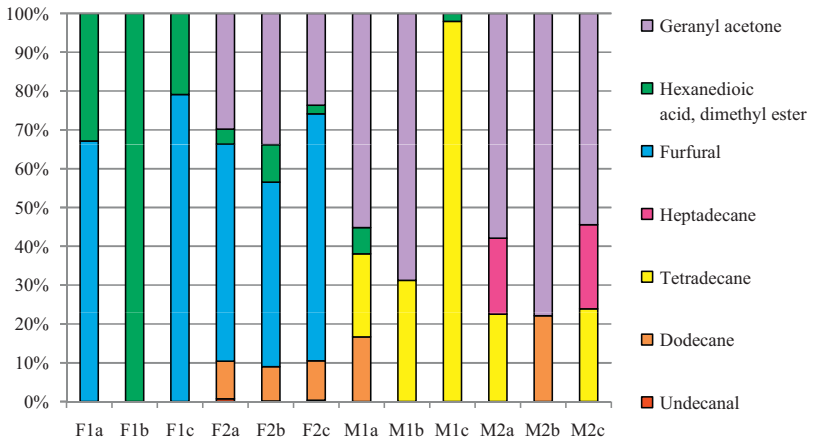

Fig. 13. Triplicate scent profiles collected from 4 human subjects (F1, F2, M1 and M2).

prone to compound breakthrough during the sampling process as air containing VOCs is swept quickly passed the material before volatiles can be deposited. Two/three layers of material slow the air flow, preventing breakthrough, and increases the surface area onto which compounds can be trapped, thus increasing the quantity that can be analyzed. Increasing the number of layers beyond this increases surface area, but also impedes airflow to such a degree that a lower quantity is collected onto the material. The rate of airflow through 1, 2, and 4 layers of the Johnson and Johnson gauze was measured and determined to be less than 0.1 m/s for all samples, as was the airflow rates for 3 and 6 layers of the other three materials.

The greatest total amount of compound was collected using two layers of the Dukal gauze. Of the single layers, the greatest total compound recovered was by the Johnson and Johnson gauze; however this was not the case for the multi-layer experiments, in which the Dukal gauze out-performed the Johnson and Johnson gauze. A high amount of compound was also recovered from the two layers of polyester, however the reproducibility was poor. It may be that these results are related to airflow; though the airflow was too low to be measured (<0.1 m/s). For instance, it is possible that the two layers of Johnson and Johnson gauze did not perform as well because the airflow was too low and less volatiles were drawn to the STU-100. Also, the improved performance of the Dukal gauze and the polyester material may be due to a reduction in the airflow and thus a reduction in compound breakthrough. Further studies with multiple layers of different material types may shed light on the correlation between multiple layers and the scent collection performance, but are beyond the scope of this study.

3.5. Human subject sampling

Finally, the previously developed and optimized method was tested using four individuals, two male and two female (M1, M2, F1, F2). Scent profiles were successfully acquired from these individuals, in triplicate, using the Johnson and Johnson gauze pad as collection material and the lowest flow rate setting with the STU-100, previously shown to trap and/or release the greatest amount of standard compounds in single layer tests. Seven compounds, previously reported to be human scent constituents [2,3,8,13,18], were detected among the human subjects sampled and are listed in Table 6. The compounds listed in Table 6 are also color coded to correspond to Fig. 13, which depicts a visual representation of the relative ratio patterns of the seven collected VOCs. There are both qualitative and quantitative similarities and variations among the samples collected from the four subjects.

4. Conclusion

This work was conducted to scientifically evaluate the Scent Transfer Unit (STU-100) as a collection tool using five different sorbent mediums for the non-contact collection of volatile organic compounds previously reported to be present in human scent. For this study, a series of controlled odor mimic permeation systems (COMPS) were developed to deliver five standard compounds to the STU-100 at controlled rates. In an effort to reduce background contamination during sampling, a human scent collection chamber was also designed using positive air flow. It was determined that the chamber enhanced non-contact dynamic airflow sampling by decreasing the amount of background contamination, thereby improving the reproducibility of replicate samples.

Using the human scent collection chamber, volatiles were collected by the STU-100 onto five collection materials at four air flow rates, and were compared. It was found that the collection material used affected the amount of compound collected. Material with a tighter weave tended to collect a greater amount of the compounds, as the greater airflow restriction may cause less to be lost due to the breakthrough of the compounds as they were

Table 6
Human scent compounds detected in human subject samples.

	F1a	F1b	F1c	F2a	F2b	F2c	M1a	M1b	M1c	M2a	M2b	M2c
Undecanal [2,18]				x	x	x						
Dodecane [3,18]				x	x	x	x		x			
Tetradecane [3,8,13,18]							x	x		x	x	
Heptadecane [2,3,8,18]										x	x	
Furfural [3]	x	x		x	x	x						
Hexanedioic acid, dimethyl ester [3,18]	x	x	x	x	x	x	x		x			
Geranyl acetone [2,3,8,18]				x	x	x	x	x		x	x	x

passing through the collection material with the airflow. The fiber chemistry of the collection material also played a key role in the trapping and releasing of compounds, as the polyester polymer was not as efficient at trapping and/or releasing certain compounds compared to the cellulose-based cotton and rayon materials, due to differences in the molecular interactions between the volatile compounds and the molecular backbone of the sorbent materials.

Changes in the flow rate setting on the device influenced the quantity of VOCs collected, with higher flow rates generally yielding lesser amounts of VOCs, again, possibly due to compound breakthrough. When the airflow through the STU-100 is high, either due to a high flow rate setting on the STU-100 or due to the weave of the collection material, VOCs may be swept past the material due to the force of the vacuum instead of being trapped by the collection material. For this reason, the layering of collection material was tested. When multiple layers of a single material were used, the greatest amount of compound detected was by the use of an intermediate number of material layers. Overall, the polyester material trapped and/or released the least amount of standard human scent compounds whereas Johnson and Johnson and Dukal trapped and/or released the greatest amount of compounds. For single layered materials, Johnson and Johnson gauze showed the greatest amount of compounds overall but showed some variation when comparing individual compounds and flow rates. For the layered materials, the Dukal gauze trapped and/or released the greatest amount of compounds.

Spearman rank correlation was used to evaluate the similarity of replicate COMPS samplings. Dukal gauze yielded the best results of all of the materials studied, demonstrating a perfect correlation among all of the replicate samples. The scores between all replicates from the same material are 0.981 or higher for all the materials studied with the exception of polyester. These results demonstrate that collection of VOCs from the COMPS in controlled environmental conditions with the STU-100 yield reproducible VOC profiles on all materials studied with the exception of polyester.

Following optimization, non-contact dynamic airflow sampling using the STU-100 was successfully applied to the collection of VOCs from the palms of four human subjects. SPME-GC/MS analysis of the samples revealed VOC profiles for each subject.

In the future, any similar sampling devices should be carefully evaluated before use in the field as there are significant variations in collection efficiencies with changes in material(s) and flow rates through the collection materials.

Acknowledgements

The authors gratefully thank Dr. Abuzar Kabir for his assistance in preparing and revising this manuscript. The authors also acknowledge the Technical Support Working Group (TSWG) for financially supporting this work.

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